Flory-Huggins theory for the solubility of heterogeneously-modified polymers

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Many water soluble polymers are chemically modified versions of insoluble base materials such as cellulose. A Flory-Huggins model is solved to determine the effects of heterogeneity in modification on the solubility of such polymers. It is found that heterogeneity leads to decreased solubility, with the effect increasing with increasing blockiness. In the limit of extreme blockiness, the nature of the phase coexistence crosses over to a polymer-polymer demixing transition. Some consequences are discussed for the synthesis of partially modified polymers, and the experimental characterisation of such systems.

Many water-soluble polymers are made by chemically modifying insoluble base materials such as starches and gums, for example a wide class of water-soluble polymers are obtained from cellulose [1, 2]. It is often possible to vary the degree of modification of the base polymer to obtain water soluble polymers with, in principle, continuously variable properties. A basic characteristic of these polymers is their solubility, but given the essentially stochastic nature of the chemical modification step, what is the effect of heterogeneity in modification on the solubility of the resulting materials?

In the present paper, this question is approached from a theoretical point of view by setting up a Flory-Huggins model for the phase behaviour of a polymer-solvent mixture [3], where the polymers have a random degree of modification. In this approach, the issue of solubility is translated into the problem of determing the phase coexistence between a dissolved aqueous phase and an undissolved (water-poor) phase. The solubility is then formally given by the polymer concentration in the aqueous phase. Determination of the full phase behaviour for a multicomponent Flory-Huggins theory is an onerous task though, and a simpler approach is to examine the spinodal stability of the system, which can be taken to be representative of the full phase behaviour. This is the approach taken in the present paper. It is arguably more insightful than a full calculation of the phase behaviour since closed-form analytic expressions can be obtained for the spinodal stability limit. The approach taken is similar to models for the phase behaviour of random block copolymer melts which have been developed in the past [4, 5, 6]. There has been rather little work though on random copolymers which also include a solvent, apart from a brief example described by Sollich *et al* [7].

In the present model, it is supposed that the system comprises a large number of species of polymers i with differing degrees of modification $0 < \alpha_i < 1$ and concentrations ρ_i. For simplicity, length polydispersity is neglected, and all the polymers are assumed to have the same number N of segments. The system is then described by the following (mean field) Flory-Huggins free energy density,

$$f = \sum_i \rho_i \log \rho_i + (1-\phi) \log(1-\phi) + \chi(\phi-\eta)(1-\phi), \quad (1)$$

where ϕ is the total polymer segment concentration and η is the concentration of chemically modified segments, given respectively by $\phi = N \sum_i \rho_i$ and $\eta = N \sum_i \rho_i \alpha_i$. The first term in Eq. (1) is the ideal free energy of mixing. The second term is the usual Flory-Huggins configurational chain entropy. The third term is the free energy cost of the unmodified polymer segments at a concentration $\phi - \eta$ coming into contact with solvent (water) at a concentration $1 - \phi$. Typically one expects $\chi > 1/2$ for this interaction, to represent the repulsion between unmodified segments and water which leads to phase separation of unmodified polymers. To keep the model simple, this is the only χ-parameter that is retained in the problem.

Eq. (1) has the structure of a *moment free energy*, since the excess free energy, comprising the second and third terms, only depends on ϕ and η which are *moment densities*. Such a system can be analysed using the methods developed by Sollich and coworkers [7, 8, 9, 10]. In particular, Ref. [10] describes how the spinodal stability conditions for systems with an excess free energy can be expressed in terms of moment densities, generalising various truncation theorems obtained by earlier workers [11, 12]. I now summarise the relevant results, translated into terms suitable for the present problem. Let us consider such a system with a free energy $f = \sum_i \rho_i \log \rho_i + f^{(\text{ex})}(\phi^{(1)} \ldots \phi^{(n)})$, where the excess free energy depends on moment densities of the form $\phi^{(r)} = \sum_i \rho_i w_i^{(r)}$ $(r = 1 \ldots n)$, with the $w_i^{(r)}$ being species-dependent weights. The fundamental idea is that the moment densities can be treated as effective species concentrations. In particular, it can be proved that spinodal stability corresponds to the positive-definiteness of the matrix $\mathbf{M}$ of second partial derivatives of the free energy with respect to the moment densities. In Ref. [10] it is shown that $\mathbf{M} = \mathbf{M}_{\text{id}} + \mathbf{M}_{\text{ex}}$ where $(\mathbf{M}_{\text{id}}^{-1})_{rs} = \sum_i \rho_i w_i^{(r)} w_i^{(s)}$ and $(\mathbf{M}_{\text{ex}})_{rs} = \partial^2 f^{(\text{ex})}/\partial \phi^{(r)} \partial \phi^{(s)}$. The limit of spinodal stability is given by $\det \mathbf{M} = 0$. This condition usually corresponds to the vanishing of a single eigenvalue of $\mathbf{M}$, with an eigenvector $\Delta \phi^{(s)}$ that satisfies $\sum_s (\mathbf{M})_{rs} \Delta \phi^{(s)} = 0$. It is shown in Ref. [10] that the spinodal instability direction in the space of species concentrations is given by $\Delta \rho_i = \sum_{rs} \rho_i w_i^{(r)} (\mathbf{M}_{\text{id}})_{rs} \Delta \phi^{(s)}$.

For the present problem, there are two moment densities ϕ and η, defined respectively with $w_i^{(1)} = N$ (a con-

stant) and $w_i^{(2)} = N\alpha_i$ (the number of modified groups on the ith species). Application of the above theory to Eq. (1) leads to

$$\mathbf{M}_{\rm id}^{-1} = N^2 \begin{pmatrix} \sum_i \rho_i & \sum_i \rho_i \alpha_i \\ \sum_i \rho_i \alpha_i & \sum_i \rho_i \alpha_i^2 \end{pmatrix} \qquad (2)$$

and

$$\mathbf{M}_{\rm ex} = \begin{pmatrix} (1-\phi)^{-1} - 2\chi & \chi \\ \chi & 0 \end{pmatrix}. \qquad (3)$$

After some algebra the condition $\det \mathbf{M} = 0$ reduces to

$$\frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi(1 - \langle\alpha\rangle) - \chi^2 N\phi(\langle\alpha^2\rangle - \langle\alpha\rangle) = 0, \qquad (4)$$

where

$$\langle\alpha\rangle = \sum_i \rho_i \alpha_i / \sum_i \rho_i, \quad \langle\alpha^2\rangle = \sum_i \rho_i \alpha_i^2 / \sum_i \rho_i. \qquad (5)$$

I emphasise that, despite being remarkably simple, Eq. (4) is exact.

One already reaches a significant conclusion from this. The first three terms in Eq. (4) are what one would expect from standard Flory-Huggins theory [3], with an effective χ-parameter given by the product of the original χ-parameter and the fraction $1 - \langle\alpha\rangle$ of unmodified segments. These terms therefore take account of the *mean* degree of modification. The final term in Eq. (4) is a correction due to the heterogeneity. Since the variance $\langle\alpha^2\rangle - \langle\alpha\rangle^2$ is positive, this term is always negative. The effect is that heterogeneity in modification *reduces* the solubility, over and above what would be expected from the mean degree of modification.

To make further progress, it is convenient to specify a model for the distribution of the α_i. In particular, such a model can be used to examine the effect of blockiness in modification which is expected to play an important role. In previous work on random block copolymers [4, 5], a Markov model was used to characterise the correlations between different kinds of segments. Whilst such a model may be appropriate for the stochastic nature of the synthetic route for such random block copolymers, as discussed below it is probably not appropriate in the present case. I therefore consider instead a very simple model for the heterogeneity in which the modified segments occur in blocks of size M, where $1 < M < N$. In this model, it is supposed that each block has an equal probability p of being modified, and there are no further correlations. Then, for any particular species, $\alpha_i = (1/N)\sum_{j=1}^{N/M} M\epsilon_{ij}$ where j labels the blocks, and ϵ_{ij} is zero or one with probability $1 - p$ and p respectively. Thus the α_i are drawn from scaled binomial distribution, with

$$\langle\alpha\rangle = p, \quad \langle\alpha^2\rangle - \langle\alpha\rangle = (M/N)\,p(1-p). \qquad (6)$$

Eq. (4) becomes

$$\frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi(1-p) - \chi^2 M\phi p(1-p) = 0. \qquad (7)$$

This is a quadratic equation for χ and the appropriate root is

$$\chi = \frac{1}{M\phi p}\Big[\Big\{1 + \frac{M\phi p}{1-p}\Big(\frac{1}{N\phi} + \frac{1}{1-\phi}\Big)\Big\}^{1/2} - 1\Big]. \qquad (8)$$

I now examine the consequences of this result.

The formal limit $M \to 0$ corresponds to a vanishing variance and a completely uniform distribution of modified segments, as though each monomer has undergone an identical fractional modification by a fraction p, rather than being modified or not with probability p and $1 - p$. As noted already above, this limit corresponds to simple Flory-Huggins theory with an effective χ-parameter equal to $\chi(1-p)$. For large N, this indicates the absence of phase separation for $\chi(1-p) < 1/2$ or $p > 1 - 1/(2\chi)$.

Now let us consider Eq. (8) for block size $M = 1$. In this case, individual segments are modified randomly with no correlations. For $M = 1$ and large N in Eq. (8), there are two behaviours depending on the value of p. For $p < 4/5$, there is an absence of phase separation for $\chi(1-p) < 1/2$, just as for the $M \to 0$ limit. For $4/5 < p < 1$, the behaviour is more complicated. To be precise, the location of the minimum value of the $\chi(\phi)$ spinodal shifts from $\phi_{\rm min} \sim N^{-1/2}$ for $p < 4/5$ to a non-vanishing $0 < \phi_{\rm min} < 1$ for $p > 4/5$ (it is the examination of Eq. (8) in the limit $\phi \sim N^{-1/2}$ that gives the cross over point $p = 4/5$). The change in behaviour can be seen for the $M = 1$ curves (dashed lines) in Fig. 1 and is shown explicitly in the upper plot of Fig. 2.

Let us next consider the limit of extreme blockiness $M = N$. This limit is strikingly different from the $M = 1$ case. For large N and $p > 0$, one can show that there is an absence of phase separation only for $\chi\sqrt{Np(1-p)} < 2$. In the large N limit, this inequality is always violated, indicating that the system *always* has a tendency to undergo phase separation in the limit of extreme blockiness. Since the unmodified polymer system itself only phase separates for $\chi > 1/2$, this suggests that the phase separation has the nature of a polymer-polymer demixing transition rather than a solvent-driven phase separation. This insight is confirmed by analysis of the spinodal instability direction below.

For large N and general M in Eq. (8), one would expect that the above two cases represent the two classes of behaviour. In the first case $M \ll N$ and the behaviour is similar to the $M = 1$ limit where individual segments are randomly modified. In the second case, $M \propto N$ and the behaviour is similar to the $M = N$ limit of extreme blockiness. Fig. 1 shows typical spinodal curves calculated from Eq. (8) for various values of p and M. The location of the minimum $(\phi_{\rm min}, \chi_{\rm min})$ of the spinodal curves can be numerically determined, and Fig. 2 shows how this depends on p.

The results show firstly that for $M \ll N$, increasing p leads to increasing solubility as the value of χ required to reach the spinodal instability is increased. Moreover, a decrease in solubility between a uniform model ($M \to 0$) with no heterogeneity, and a model with fine-grained
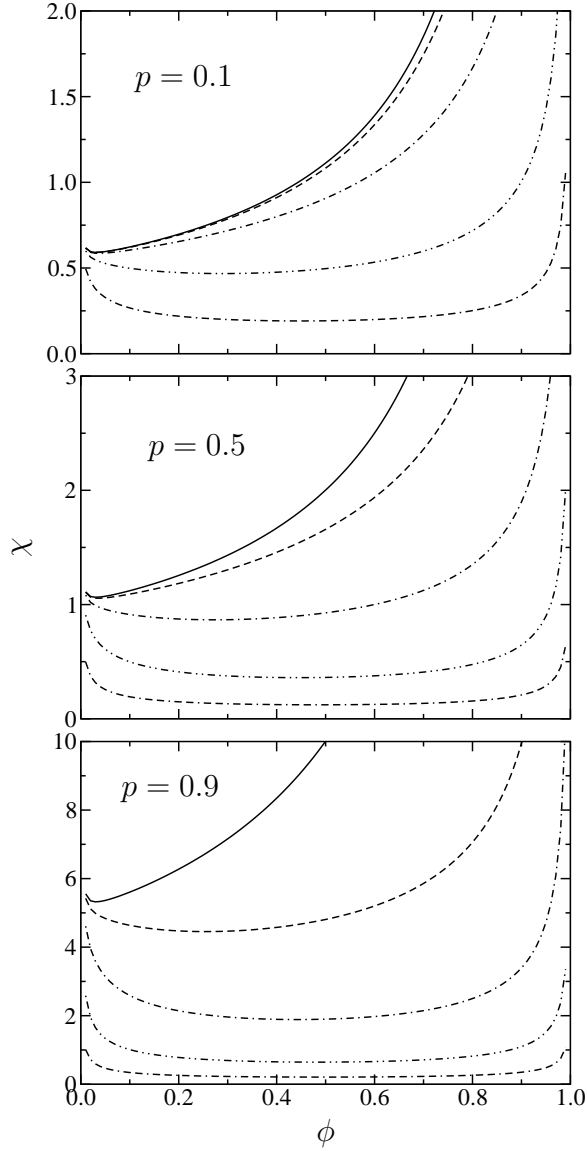
FIG. 1: Spinodal curves calculated from Eq. (8) for polymers of length $N = 10^3$, for three values of the mean degree of modification p, and for block sizes $M \to 0$ (uniform limit, solid line), $M = 1$ (dashed line), $M = 10$ (dash-dot line), $M = 100$ (dash-dot-dot line) and $M = 10^3$ (dash-dash-dot line). The system is spinodally unstable above the indicated curves. Note the change in shape of the $M = 1$ curves: for $p = 0.1$ and 0.5 the minimum is at $\phi \to 0$, whereas for $p = 0.9$ the minimum is at $\phi \approx 0.25$.

blockiness ($M = 1$), is apparent. The major effect arises as $M \to N$ though, where the tendency for phase separation is greatly enhanced.

The above analysis is augmented considering the spinodal instability direction associated with the spinodal stability limit which can provide a useful mechanistic insight. As explained above, the spinodal instability direction is characterised by the eigenvector that corresponds to the vanishing eigenvalue responsible for the vanish-
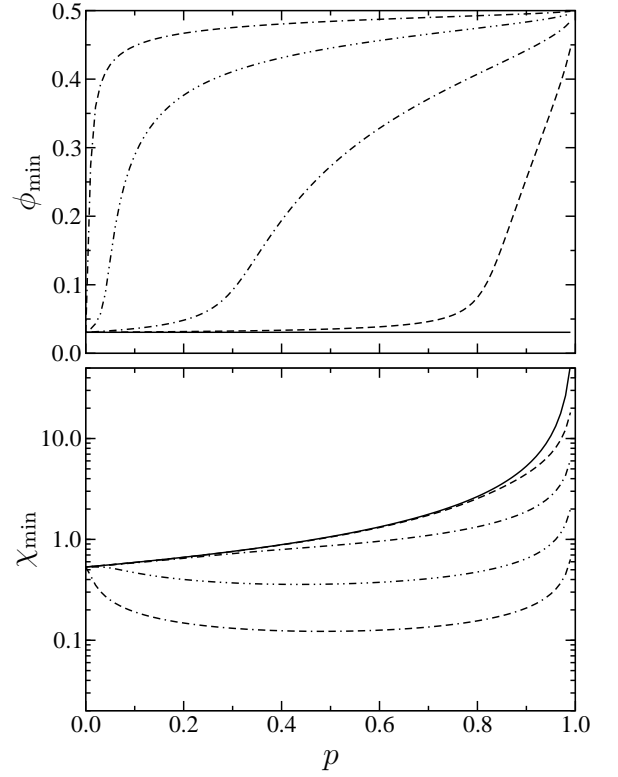

FIG. 2: The location of the numerically determined minimum of the spinodal curves from Eq. (8) is plotted as a function of p, for polymers of length $N = 10^3$ and block sizes $M \to 0$ (uniform limit, solid line), $M = 1$ (dashed line), $M = 10$ (dash-dot line), $M = 100$ (dash-dot-dot line) and $M = 10^3$ (dash-dash-dot line). For $M = 1$ (dashed line) the upper plot shows clearly that $\phi_{\min} \approx N^{-1/2} \approx 0.03$ only holds for $p \lesssim 4/5 = 0.8$.

ing spinodal determinant. For the present problem, from Eqs. (2)–(3), one finds the instability direction is characterised by

$$\Delta \eta \, / \, \Delta \phi = \langle \alpha \rangle - \chi N \phi (\langle \alpha^2 \rangle - \langle \alpha \rangle^2) \qquad (9)$$

The corresponding spinodal instability direction in the space of species concentrations is

$$\begin{aligned} \frac{\Delta \rho_i}{\rho_i} &= \frac{\langle \alpha^2 \rangle \Delta \phi - \langle \alpha \rangle \Delta \eta + \alpha_i (\Delta \eta - \langle \alpha \rangle \Delta \phi)}{\phi(\langle \alpha^2 \rangle - \langle \alpha \rangle^2)} \\ &= \frac{\Delta \phi}{\phi} \Big(1 + \chi N \phi (\langle \alpha \rangle - \alpha_i) \Big) \end{aligned} \qquad (10)$$

where the second line follows by inserting the result for the ratio $\Delta \eta / \Delta \phi$. These results should be evaluated on the spinodal. They are all exact, for an arbitrary distribution of α_i.

For the instability direction to lie along a pure dilution line, one should have $\Delta \rho_i / \rho_i$ independent of species i. One can conclude that this only happens if $\Delta \eta / \Delta \phi = \langle \alpha \rangle$, in other words if the variance $\langle \alpha^2 \rangle - \langle \alpha \rangle^2$ vanishes. In such a case, the phase transition is purely associative,

or solvent-driven, meaning that the compositions of the coexisting phases remain the same ($\Delta\rho_i/\Delta\phi = \rho_i/\phi$).

If one specialises to the model of blockiness described above by inserting the value of χ corresponding to the spinodal stability limit, the instability direction becomes

$$\frac{\Delta\eta}{p\Delta\phi} = 1 - \frac{1-p}{p}\Big[\Big\{1 + \frac{M\phi p}{1-p}\Big(\frac{1}{N\phi} + \frac{1}{1-\phi}\Big)\Big\}^{1/2} - 1\Big].$$
(11)

This confirms that the spinodal instability lies along a dilution line ($\Delta\eta/\Delta\phi = \langle\alpha\rangle = p$) only in the limit $M \to 0$ which formally corresponds to a vanishing variance. For $M = 1$ (and $M \ll N$ in general) the phase transition has a mixed character. The interesting case occurs when $M = N$ (or $M \propto N$ in general) for which $\Delta\eta/\Delta\phi \sim (-)N^{1/2}$ in the limit of large N. One can write this as $\Delta\phi/\Delta\eta \to 0$ as $N \to \infty$. This shows that the phase transition tends towards being purely segregative, meaning that the overall polymer concentration in coexisting phases remains the same ($\Delta\phi = 0$). This confirms the suggestion above, that in the limit of extreme blockiness, the system tends towards a segregative polymer-polymer demixing transition.

Let us now try to draw some conclusions. The main effect of randomness is to reduce the solubility of partially-modified polymers beyond what would be expected from the mean degree of modification. The extent to which this occurs depends on the blockiness in substitution. For fine-grained blockiness, the phase behaviour is expected to be similar to a system for which there is no randomness, albeit with a somewhat reduced solubility. For coarse-grained blockiness, where the block size is comparable to the polymer length, the nature of the phase transition changes to a polymer-polymer demixing transition. In this situation, one expects that the modified polymers (being almost fully modified) will partition into the aqueous phase, leaving the unmodified polymers behind.

The reason for considering the two extreme kinds of blockiness is now clearer: namely one can envisage two different mechanisms of chemical modification (this is the reason why a Markov model for the distribution of modified segments has not been used). Fine-grained blockiness would arise if monomers are equally accessible to the modifying agent, irrespective of their surroudings. If this cannot be achieved in a one-step process (for the reason described below) it could perhaps be achieved in a two-step process, by fully modifying the polymers then removing a random fraction of the derivative groups. Extreme blockiness on the scale of the polymer chain itself would arise if the modifying agent was present only in the aqueous phase, and as such only able to access polymer which had already been solubilised. This would lead to a mixture of polymers which were either fully modified, or remained unmodified and insoluble. The process of modification of insoluble polymers could still be initiated because the modifying agent is able to access the tiny proportion of the insoluble polymer segments which lie at the interface between the insoluble and aqueous phases. Experimentally, confirmation of the scenario of extreme blockiness would be given by measuring the mean degree of modification for the *dissolved* polymers. One should find that this is much in excess of the apparent mean degree of modification.

In the calculation, the major effect arises from inter-chain rather than intra-chain heterogeneities. The model is not sophisticated enough to take account of the solution structures such as micelles or mesophases that could form for blocky polymers with block sizes $M \gg 1$ but still $M < N$ (for example, diblock copolymers). Such polymers would be expected to have greater solubilities than would be predicted from the Flory-Huggins theory since the hydrophobic groups can be buried in micelles or other solution structures. The present theory could be extended to discuss these inhomogeneous situations using a Landau approach developed for random block copolymers [4, 5, 6]. For the mechanistic routes discussed above though, it is difficult to envisage that polymers with intermediate block sizes could arise very easily. I therefore expect that the general conclusions will remain.

Finally I note that in principle the above model for the phase behaviour could be combined with a model for the chemical modification reaction, to obtain a theory for reaction-induced solubility. However, one needs to take great care to capture the kinetics correctly [13].

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